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(54) METHOD OF MANUFACTURING LAMINATED FILMS

(71) We, HENKEL KOMMANDITGESELLSCHAFT AVF AKTIEN., a German Company, of 67 Henkelstrasse, 4000 Duesseldorf-Holthausen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of manufacturing laminated films by using solvent-free adhesives based on polyfunctional isocyanates and polyfunctional primary amines.

Laminated films are generally manufactured by means of laminating adhesives which contain solvents and which are applied to a web of film by means of rollers. After the solvent has evaporated, the web is united with the second web under pressure which is applied for a short period of time. In this method, known as "dry laminating", the adhesives used are almost exclusively solvent-containing polyurethane systems in the form of moisture-hardening isocyanate end position prepolymers or two-component polyol/polyisocyanate mixtures. Recent restrictions with respect to the emission of solvents into the atmosphere render it necessary to perform expensive processing steps for the absorption or after-burning of the solvent/air mixture.

By practice of the present invention there is provided, for the purpose of manufacturing laminated films, an adhesive system which is free from solvents and which can thus be processed without the risk of fire or explosion and which also permits a more economical method of manufacture.

By practice of the present invention there is also provided a method of manufacturing laminated films which produces clear, adherent laminated films at low technological expense.

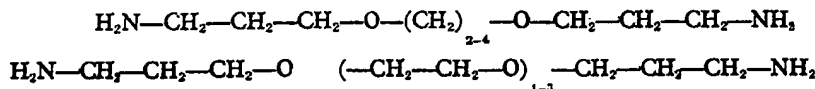
According to the present invention there is provided a method of manufacturing laminated films using solvent-free isocyanate adhesives in which a polyether carrying at least two end position isocyanate groups is applied to one of two films to be bonded together, and at least one compound which carries at least two end position primary amino groups, and whose molecular weight is from 300 to 2000, is applied to the other film, the molar ratio of isocyanate groups to amino groups being from 1:1 and 2.0:1, the two components together forming a coating thickness of from 1.0 to 6 μm , and the two layers of film are pressed together for a period of time sufficient to effect primary adhesion.

At least bifunctional isocyanates suitable for the method in accordance with the present invention can be produced by reacting anhydrous polyether diols with at least bifunctional isocyanates in a manner known per se. Preferred polyether diols are derived from glycols containing 2 to 4 carbon atoms. Consequently, polyethylene- and/or polypropylene glycol and/or polytetramethylene ether glycol (produced by ring-opening polymerisation of tetrahydrofuran) are suitable. Relatively low molecular weight isocyanates, such as hexamethylene diisocyanate, isophorone diisocyanate, toluylene diisocyanate (isomeric mixture) and others, are primarily suitable for the reaction with the polyether diols. Care should be taken that the isocyanate compounds obtained do not exceed a viscosity of approximately 8000 to 9000 cP during processing. If required, this reaction component can also be applied with slightly increased temperatures of up to 50 to 60°C. In general, however, temperatures of from 20 to 30°C will be preferred.

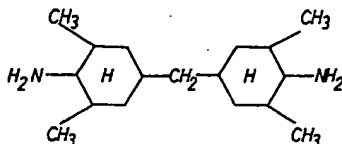
The second reaction component used for the method in accordance with the invention is an at least bifunctional primary amine. It can be built up from the

same basic component, i.e. polyether diols. Advantageously, acrylonitrile is added to the polyether diols. This adduct is then hydrogenated in a known manner, primary amino groups being formed from the nitrile groups. Polyether glycols, derived from polyethylene glycol, polypropylene glycol and polytetramethylene ether glycol having a molecular weight between substantially 200 and 1500, most preferably 300 to 1000, are preferred for the manufacture of the two reaction components of the solvent-free laminating adhesive.

Furthermore, it is possible to proceed from relatively low molecular weight diamines having a chain length of from 2 to 18 carbon atoms which may also be partially replaced by oxygen atoms, and to react these diamines with compounds containing at least two functional groups which are capable of reaction with an amine (chain lengthening). Amines of this type are, for example:



or alternatively

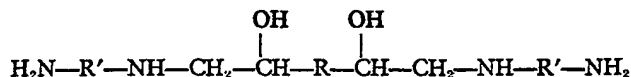


The functional groups may be epoxide- or isocyanate radicals or α,β -unsaturated esters or halogen atoms. The OH groups, secondary amino groups or urea groupings formed during this reaction or the ester groupings introduced promote the adhesion or strength of the bonded joint.

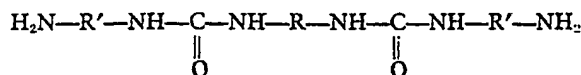
In the case of a diepoxide or diglycidyl compound:



wherein R is an aliphatic or cycloaliphatic radical containing up to approximately 25 carbon atoms, such as methylene, ethylene, propylene, neopentyl, hexylene, dodecylene, cyclohexylene, dicyclohexyl, methylene dicyclohexyl or, alternatively diethylene or triethylene glycol ether radical, and the diprimary amine corresponds to the general formula $\text{H}_2\text{N}-\text{R}'-\text{NH}_2$, wherein R' represents, for example, an ethylene-, butylene-, hexylene-, diethylene glycol ether-, dipropylglycol ether-, or, alternatively, triethylene glycol ether radical, one obtains compounds, containing two end position primary amino groups, of the general formula:

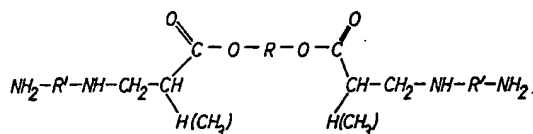


In the case of chain lengthening with isocyanates, such as toluylene diisocyanate, hexamethylene diisocyanate and, isophorondiisocyanate, one obtains compounds, containing two end position amino groups and urea groups, of the general formula:



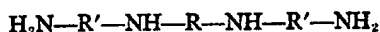
in which R' again has the same significance as above, and R represents the isocyanate used.

When using (meth) acrylic acid esters (for example tri- or tetraethylene glycol di(meth)acrylic ester) for chain lengthening, one obtains compounds of the general formula:



in which R' again has the same significance as above, and R represents the dialcohol radical of the (meth) acrylic ester, i.e. the tri-, or tetraethylene glycol ether radical in the case mentioned by way of example. It will be appreciated that one can also proceed from other di(meth)acrylic acid esters of glycols, such as ethylene glycol, propylene glycol, butylene glycol and, decane diol.

Finally, it is also possible to effect a chain link with α,ω -dihalides, this being effected in accordance with the same principle in a known manner. In this case, compounds of the general formula:



are produced, in which R represents a radical of up to 12 carbon atoms and which can optionally contain oxygen, such as in the case of the tetraethylene glycol ether radical or tripropylene glycol ether radical, and R' has the same significance as before.

The ratio of diprimary amines to the chain-lengthening agent should be chosen such that approximately 1 mol of difunctional epoxide, isocyanate, (meth)acrylic ester or dihalide is allotted to 2 mol of amine. The reaction forms substantially the desired compounds containing at least two end position primary amino groups and having a molecular weight of substantially 300 to 2000. Advantageously, the viscosity of the amine component is somewhat less than that of the isocyanate component. It has proved to be practicable to work towards a viscosity of approximately 50 to 1200 cP at 20 to 30°C.

In practice the two reaction components are applied to the films by means of rollers such that the molar ratio of the isocyanate groups to the amino groups lies between substantially 1:1 and 2:1.0. The quantity is otherwise measured such that a film of adhesive having a total thickness of 1.0 to 6.0 μm is formed.

Also in practice the surfaces of the films coated with the two components are pressed together between a pair of rollers which may also be partially heated. Adequate primary adhesion (initial adhesion) is formed on the way to the rolling-up arrangement and, if required, can be increased by applying heat by, for example, hot air.

The method in accordance with the present invention enables the laminating operation to be carried out at relatively high speeds. There is no need to use drying channels. After the films have been pressed together, the webs do not slip or slide relative to one another and partial delamination does not even occur. After the films have been wound onto rolls, the films have to be stored for substantially 3 to 7 days at room temperature according to the thickness of the film of adhesive and the reactivity of the reactants. The final strength is formed during this period of time. The peel strength of the laminates obtained is usually so high that it is impossible to delaminate them without tearing the material.

The peel strength is measured by pulling apart a 15 mm. width of film clamped in a tearing machine the angle between the two layers being pulled apart in the tearing machine being 180°. The measurements are made at room temperature (i.e. approximately 21 to 23°C.) ten measurements being made in each case and the two extreme values being discarded the remaining eight values being quoted in terms of the range they encompass.

Laminatd films made from the components polyethylene (pretreated), polypropylene (pretreated), cellulose hydrate in a lacquered and non-lacquered form, polyethylene terephthalate, polycaprolactam, aluminium and other metals, can be manufactured by means of the method in accordance with the present invention.

The present invention will now be further illustrated by reference to the following examples:

Example 1

Component A: Isocyanate adduct from polypropylene glycol (average molecular weight 410) and trimethylhexamethylene diisocyanate in the molar ratio 1:2 (molecular weight 830).

Content of free isocyanate groups: 10.1%

Viscosity at 25°C: 3,500 cP (Brookfield)

Component B: Aminopropylated polypropylene glycol (average molecular weight 410), obtained by adding acrylonitrile to the glycol and subsequent catalytic hydrogenation (theoretical molecular weight 524).

Amine number: 170—180

Viscosity: 60 cP (Brookfield)

2.5 g of component A are applied to 1 square metre of polyethylene film of low density which has been pretreated by corona discharge (film thickness 50 μm), and 1.56 g of the component B are applied to 1 square metre of polyester film (film thickness 12 μm), the molar ratio of isocyanate groups to amino groups being 1.2:1, this corresponding to coating thicknesses of approximately 2.5 and 1.56 μm respectively, and the coated sides of the films are joined together by means of rollers. The film of adhesive exhibited spontaneous initial adhesiveness, and a peel strength of 3 to 5 $\frac{1}{2}$ p/15 mm was measured 30 seconds after bonding (draw-off speed 100 mm/min). After four days storage, it is impossible to delaminate the film without tearing the material.

Example 2

Component A: Isocyanate adducts from polypropylene glycol (average molecular weight 630) and trimethylhexamethylene diisocyanate in the molar ratio 1:2 (molecular weight 1050)

Content of free isocyanate groups: 8.0%

Viscosity at 25°C: 5,000 cP (Brookfield)

Viscosity at 50°C: 1,000 cP (Brookfield)

Component B: Aminopropylated polypropylene glycol (average molecular weight 630), obtained by adding acrylonitrile to the glycol and subsequent catalytic hydrogenation (theoretical molecular weight 744).

Amine number: 142

Viscosity: 130 cP (Brookfield)

1.0 g of component A is applied to 1 square metre of pretreated polyethylene film (film thickness 50 μm), and 0.74 g of component B are applied to 1 square metre of cellulose glass film (film weight 31.5 g/m²), molar ratio of isocyanate groups to amino groups being 1.02:1, this corresponding to coating thicknesses of approximately 1 and 0.75 μm respectively, and the coated sides are united by means of rollers. The laminated film is then immediately heated to 50°C for 10 seconds. The peel strength subsequently measured is 5 to 6 kp/15 mm (draw-off speed 100 mm/min.). After four days storage, it is impossible to delaminate the film without destroying the material.

Example 3

Component A: Isocyanate adduct from polytetramethylene ether glycol (average molecular weight 980) and toluylene diisocyanate in the molar ratio 1:2 (molecular weight 1328)

Content of free isocyanate groups: 6.33

Viscosity at 25°C: 7,000 cP (Brookfield)

Component B: Amine in accordance with Example 1 1.38 g of component A are applied to 1 square metre of pretreated polyethylene film (film thickness 50 μm) and 0.6 g of component B are applied to 1 square metre of polyamide film (film thickness 60 μm), approximate molar ratio of isocyanate groups to amino groups being 1.1:1, corresponding to a coating thickness of 1.38 and 0.6 μm , and the coated sides of the film are united by means of rollers. The glued film is heated to 50°C for a short period of time. The peel strength subsequently measured is 8 to 10 kp/15 mm (draw-off speed 100 mm/min.). After four days storage, it is impossible to delaminate the film without destroying the material.

WHAT WE CLAIM IS:—

1. A method of manufacturing laminated films using solvent-free isocyanate adhesives, which comprises applying a polyether carrying at least two end position

isocyanate groups to one of two films to be bonded together, and applying at least one compound which carries at least two end position primary amino groups, and whose molecular weight is from 300 to 2000, to the other film, the molar ratio of isocyanate groups to amino groups being from 1:1 to 2.0:1, the two components together forming a coating thickness of 1.0 to 6 μm , and the two film surfaces produced being pressed together for a period of time sufficient to effect primary adhesion.

2. A method as claimed in Claim 1, in which the reaction products of polyethers with acrylonitrile, which have subsequently been hydrogenated, are used as the compounds carrying at least two primary amino groups.

3. A method as claimed in Claim 1 or Claim 2, in which the manufacture of the polyethers containing isocyanate groups or amino groups is based on polyethylene- or polypropylene- or polytetramethylene ether glycol having a molecular weight of from 200 to 1500.

4. A method as claimed in Claim 3, in which the manufacture of the polyethers containing isocyanate groups or amino groups is based on polyethylene- or polypropylene- or polytetramethylene ether glycol having a molecular weight of 300 to 1000.

5. A method as claimed in any one of Claims 1 to 4, in which the film surfaces produced are pressed together between a pair of rollers.

6. A method as claimed in Claim 5, in which the rollers are partially heated.

7. A method of manufacturing laminated films using isocyanate adhesives substantially as hereinbefore described and with reference to any one of the Examples.

8. A laminated film whenever produced by a method as claimed in any one of Claims 1 to 7.

W. P. THOMPSON & CO.,
Coopers Buildings,
12, Church Street,
Liverpool, L1 3AB.
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